



# Catalytic activity for methane combustion of the perovskite-type $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ oxide prepared by the urea decomposition method

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## ABSTRACT

Four methods were adopted to prepare perovskite-type oxide with molar ratio of  $\text{La}/\text{Sr}/\text{Co} = 0.9/0.1/1.0$ . The oxide prepared by the urea decomposition method showed the highest catalytic activity for methane combustion and a good durability at  $600^\circ\text{C}$  for 90 h. Surface structure features of this oxide were discussed by use of XPS data. This method was further applied to prepare other perovskite oxides with nominal degree of substitution  $x = 0.0, 0.2$  and  $0.3$ . Relation of catalytic activity with degree of substitution was discussed in view of cooperation of surface lattice oxygen vacancy with surrounding cobalt ions at lower oxidation states.

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## 1. Introduction

Catalytic combustion of hydrocarbons is an important technology both for energy production and for environmental pollution abatement. For heat generation process using natural gas as fuel, catalytic combustion instead of the conventional combustion has several advantages of such as high efficiency and lower temperature which effectively suppresses thermal  $\text{NO}_x$  formation [1]. The mostly used catalyst for combustion of natural gas is the supported palladium catalyst, which is suitable at low and medium temperatures. Active phase of this catalyst is palladium oxide in oxidizing atmosphere [2]. At temperature above about  $850^\circ\text{C}$ , palladium oxide tends to decompose into metallic palladium and shows a steep drop in activity [1,3]. For high temperature combustion Arai and co-workers developed hexaaluminate catalysts [4–6].

The supported noble metal catalysts such as  $\text{Pd}/\text{Al}_2\text{O}_3$  and  $\text{Pt}/\text{Al}_2\text{O}_3$  or their combination with Rh or Ir have high ability to activate both the C–H and O–O bonds, and show high activity even below  $350^\circ\text{C}$  [7]. But they are expensive and have a sintering tendency above  $500^\circ\text{C}$  [8]. Perovskite-type mixed oxides are less expensive and often thermally more stable than noble metals, therefore become candidates to substitute for the noble metal catalysts [9–11]. Perovskite-type oxide catalysts are also applicable at low and medium temperatures, since high temperature leads

to a reduced surface area below about  $2\text{ m}^2/\text{g}$ . The perovskite-type mixed oxide has a specific structure with general formula  $\text{ABO}_3$ , where lanthanide elements are at the A site position and first row transition metals at the B site usually. Recently Pd-perovskites were reported [12–16]. Under oxidizing atmosphere Pd element inserted in the B site, and segregated out of the lattice site under reducing atmosphere forming fine particles on the surface of the perovskite oxide. This self-regenerative behavior allows the Pd-perovskite have a good durability for automotive emission control.

It has been known that preparation method has a great influence on activity in catalytic combustion of the perovskite-type oxide. Forni et al. tested several methods, i.e., sol–gel method using citric acid, EDTA method as well as ball-milling technique, to prepare  $\text{LaMnO}_3$  and  $\text{LaCoO}_3$  catalysts [17]. It is found that the sol–gel prepared sample had the highest activity for methane combustion, though thermal resistance was insufficient for high temperature application. Flame spray pyrolysis can be used to prepare perovskites with good thermal stability, but the apparatus needed for preparation is complicated [18]. In comparison, the citrate method seems simple and easy to obtain single phase perovskites at relatively low calcination temperatures. On the other hand, preparing perovskite on/in a support was also tried to improve catalytic activity for methane combustion. Delmon et al. prepared  $\text{LaCoO}_3$  perovskites on  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  support by means of impregnation method using nitrate solution or citrate solution of the corresponding metallic ions [19]. A higher reaction rate per perovskite weight was observed at low loadings when compared to bulk  $\text{LaCoO}_3$  sample. Cao and co-workers prepared highly crystalline  $\text{LaCoO}_3$  perovskite particles in the host pores of mesoporous SBA-15 silica

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by a novel microwave-assisted process and found a high catalytic activity for methane oxidation [20].

In the present work, the urea decomposition method was adopted to prepare perovskite-type  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  oxides ( $x = 0.0, 0.1, 0.2, 0.3$ ). We had applied the urea decomposition method to prepare spinel-type  $\text{MgFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  oxides, which exhibited higher activities for oxidative dehydrogenation of ethylbenzene in comparison with those samples obtained by citrate method and precipitation methods [21]. To make a comparison with the urea decomposition method, citrate method and two precipitation methods were also adopted in this work to prepare the cobaltite perovskites. It is found that the perovskite-type oxide (with molar ratio of  $\text{La}/\text{Sr}/\text{Co} = 0.9/0.1/1.0$ ) prepared by the urea decomposition method had the highest catalytic activity and a good thermal durability for methane combustion.

## 2. Experimental

### 2.1. Catalyst preparation

Nitrates of the metallic ions ( $\text{La}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ) of analytical grade were used to prepare the perovskite-type  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.0, 0.1, 0.2, 0.3$ ) oxides. At first the required amounts of the nitrates following the nominal composition were weighed and put into a beaker, and then an amount of distilled water was added to make a solution of the mixed nitrates.

#### 2.1.1. Urea decomposition method

Added an amount of urea into the solution of the mixed nitrates prepared above at room temperature, molar ratio of urea to total metallic ions (i.e., sum of  $\text{La}^{3+}$ ,  $\text{Sr}^{2+}$  and  $\text{Co}^{2+}$ ) was set at 4.5. Kept stirring at  $85^\circ\text{C}$  for 2 h to allow the solution change into viscous slurry. The slurry was further dried in an oven at  $120^\circ\text{C}$  for 8 h. At last, the resulting solid was calcined in a muffle furnace for 5 h at  $700^\circ\text{C}$  (sometimes at  $800^\circ\text{C}$  or  $900^\circ\text{C}$  to investigate effect of calcination temperature).

#### 2.1.2. Citrate method

Added an amount of citric acid into the solution of the mixed nitrates prepared above at room temperature, molar ratio of citric acid to total metallic ions (i.e., sum of  $\text{La}^{3+}$ ,  $\text{Sr}^{2+}$  and  $\text{Co}^{2+}$ ) was set at 1.5. Kept stirring at  $85^\circ\text{C}$  for 2 h to evaporate excessive water, followed by a further drying in an oven at  $120^\circ\text{C}$  for 8 h. At last, the resulting product was calcined in a muffle furnace for 5 h at  $700^\circ\text{C}$ .

#### 2.1.3. Precipitation method with aqueous ammonia as precipitant

Added diluted aqueous ammonia drop by drop into the solution of the mixed nitrates until pH 9–10 and left it half an hour to allow precipitation completed sufficiently at room temperature. Kept stirring at  $85^\circ\text{C}$  for 2 h to evaporate excessive water, followed by a further drying in an oven at  $120^\circ\text{C}$  for 8 h. At last, the resulting product was calcined in a muffle furnace for 5 h at  $700^\circ\text{C}$ .

#### 2.1.4. Precipitation method with ammonium carbonate solution as precipitant

Added ammonium carbonate solution drop by drop into the solution of the mixed nitrates until pH 9–10 and left it half an hour to allow precipitation completed sufficiently at room temperature. Kept stirring at  $85^\circ\text{C}$  for 2 h to evaporate excessive water, followed by a further drying in an oven at  $120^\circ\text{C}$  for 8 h. At last, the resulting product was calcined in a muffle furnace for 5 h at  $700^\circ\text{C}$ .

### 2.2. Catalyst characterization

Specific surface areas of the oxides prepared above were measured at liquid nitrogen temperature by BET method (Quan-

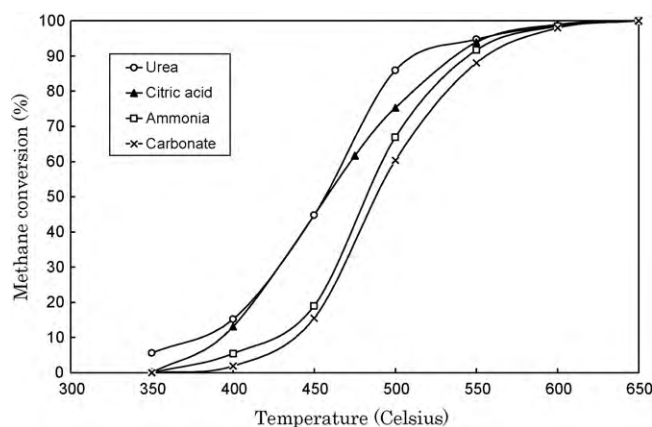


Fig. 1. Influence of preparation method on catalytic activity for methane combustion of the oxide catalyst (with molar ratio of  $\text{La}/\text{Sr}/\text{Co} = 0.9/0.1/1.0$  and calcined at  $700^\circ\text{C}$  for 5 h).

tachrome SI). The crystalline phases were recognized through powder X-ray diffraction (XRD) analysis by means of a Shimadzu diffractometer (XRD-6000). XPS analyses were performed on an X-ray photoelectron spectrometer using contaminant carbon C 1s =  $284.8\text{ eV}$  as internal standard (PHI Quantera).

### 2.3. Catalytic activity evaluations

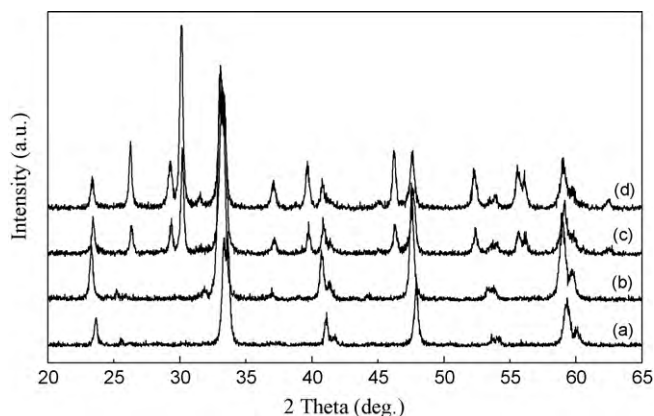
Catalytic activities for methane combustion of the oxides (granular size 40–60 mesh, 600 mg in each run) were evaluated in a fixed-bed quartz reactor (8.5 mm i.d.) under atmospheric pressure. Total flow rate of the feed gas was set at 200 ml/min, in which methane gas was 2.7 vol.%, oxygen gas 18.9 vol.% and nitrogen gas used as balance gas. Thus, weight hourly space velocity (WHSV) of the feed gas was  $20,000\text{ ml}/(\text{g}_{\text{cat}}\text{ h})$ . An on-line gas chromatograph (Kechuang, Shanghai) was used to analyze the feed and the product gases.

## 3. Results and discussion

### 3.1. Influence of preparation method

Catalytic activities for methane combustion of the oxides with molar ratio of  $\text{La}/\text{Sr}/\text{Co} = 0.9/0.1/1.0$  prepared by the four methods stated above (all calcined at the identical condition of  $700^\circ\text{C}$  for 5 h) are compared in Fig. 1. It is obvious that the oxide prepared by the urea decomposition method, denoted as (a) sample, has the best activity for methane combustion. The oxide prepared by the citrate method, denoted as (b) sample, is most approaching to the (a) sample at the conversion of ca. 45%. But in view of the initial activity and the final activity, expressed by the temperatures  $T_{10}$  and  $T_{90}$  corresponding to methane conversion of 10% and 90%, respectively, the (a) sample is superior to the (b) sample. The other two oxides prepared by the (c) method and (d) method, denoted as (c) sample and (d) sample, respectively, are inferior to the (a) and (b) samples in catalytic activity for methane combustion. Therefore, catalytic activity of the four oxides for methane combustion is in order of (a) sample > (b) sample > (c) sample > (d) sample.

Fig. 2 shows XRD patterns of the oxides prepared by the four methods (with molar ratio of  $\text{La}/\text{Sr}/\text{Co} = 0.9/0.1/1.0$  and calcined at  $700^\circ\text{C}$  for 5 h). It is seen that both the (a) method and the (b) method produced predominantly perovskite phase oxide, with a minor of  $\text{SrCO}_3$  phase observed at  $2\theta = 25\text{--}26^\circ$ . However, the (c) method and (d) method produced samples which evidently contained  $\text{La}_2\text{O}_3$  ( $2\theta = 26.1^\circ, 29.1^\circ, 30.0^\circ, 46.1^\circ, 55.4^\circ$ ) and  $\text{Co}_3\text{O}_4$  ( $2\theta = 36.9^\circ$ ) phases in addition to the main phase of perovskite. It can be considered that



**Fig. 2.** XRD patterns of the oxides (with molar ratio of La/Sr/Co = 0.9/0.1/1.0) prepared by the four methods and calcined at 700 °C for 5 h (a) urea decomposition method, (b) citrate method, (c) precipitation method using ammonia as precipitant, (d) precipitation method using carbonate as precipitant.

the uniform dispersion of the metallic ions in the precursors produced by the (a) and (b) methods is responsible for the predominant formation of the perovskite phase. Precipitation process inevitably resulted in inhomogeneous dispersion of the metallic ions in precipitate when aqueous ammonia or ammonium carbonate solution was used as precipitant. For convenience, formula  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  is still used to express the oxides prepared by the four methods in this work.

Specific surface areas of the four oxides (with molar ratio of La/Sr/Co = 0.9/0.1/1.0 and calcined at 700 °C for 5 h) are listed in Table 1. It is seen that specific surface area has no direct relation with the catalytic activity. Therefore the differences in catalytic activity of the four oxides must be due to their different surface structures. Table 2 gives surface atom compositions detected by XPS analyses for the four oxides, which excludes carbon element. The surface carbon species were originated from carbon contaminants and surface carbonates. Carbon contaminants had an intense C 1s peak calibrated at 284.8 eV in this work, and the surface carbonates showed a very weak C 1s peak around 289.5 eV. It is clear from Table 2 that all samples were Sr-rich and La-rich on surface relatively to the bulk molar ratio of La/Sr/Co = 0.9/0.1/1.0. And the (c) and (d) samples had lower surface cobalt ion concentrations in comparison to the (a) and (b) samples. Furthermore, Table 3 indicates that the (c) and (d) samples had less surface lattice oxygen, which led to molar ratio of lattice oxygen to cobalt ion in surface

**Table 1**

Specific surface areas (SSA) of the oxides prepared by the four methods (with molar ratio of La/Sr/Co = 0.9/0.1/1.0 and calcined at 700 °C for 5 h).

Samples	SSA (m <sup>2</sup> /g)
(a)	10.0
(b)	8.1
(c)	13.5
(d)	15.1

**Table 2**

Surface atom composition (%) of the oxides prepared by the four methods (with molar ratio of La/Sr/Co = 0.9/0.1/1.0 and calcined at 700 °C for 5 h) detected by XPS.

Samples	Surface atom composition (%)			
	O	Co	Sr	La
(a)	79.3	6.3	3.0	11.4
(b)	77.4	7.9	2.7	12.0
(c)	80.7	4.5	1.8	13.0
(d)	81.3	4.9	2.1	11.7

**Table 3**

Distribution of surface oxygen species (%) on the oxides prepared by the four methods (with molar ratio of La/Sr/Co = 0.9/0.1/1.0 and calcined at 700 °C for 5 h) detected by XPS.

Samples	Distribution of surface oxygen species <sup>a</sup> (%)		Surface molar ratio of lattice oxygen/cobalt ion
	Lattice oxygen	Non-lattice oxygen	
(a)	26.7	73.3	3.4
(b)	40.7	59.3	4.0
(c)	10.0	90.0	1.8
(d)	15.1	84.9	2.5

<sup>a</sup> Lattice oxygen was recognized at O 1s binding energy of 528.8 eV and the non-lattice oxygen species at O 1s binding energy of 531.3 eV.

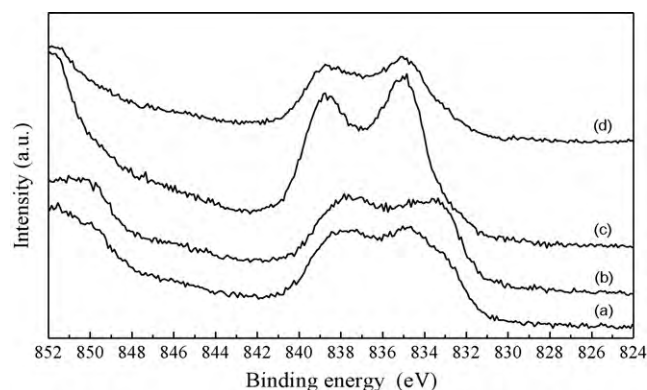
layer smaller than 3. On the other hand, Fig. 3 shows that the (c) and (d) samples had a shifted peak position of La 3d<sub>5/2</sub> binding energy to the (a) and (b) samples in X-ray photoelectron spectra. In light of the XRD results in Fig. 2, the shifted peak position of La 3d<sub>5/2</sub> binding energy supports presence of La<sub>2</sub>O<sub>3</sub> in the (c) and (d) samples [22].

In summary, the best activity of the (a) sample for methane combustion should be due to its appropriate surface structure, including concentration of surface lattice oxygen and ratio of surface lattice oxygen/cobalt ion. The appropriate surface structure allows fast rates in release and regeneration of surface active oxygen species of the (a) sample for methane oxidation.

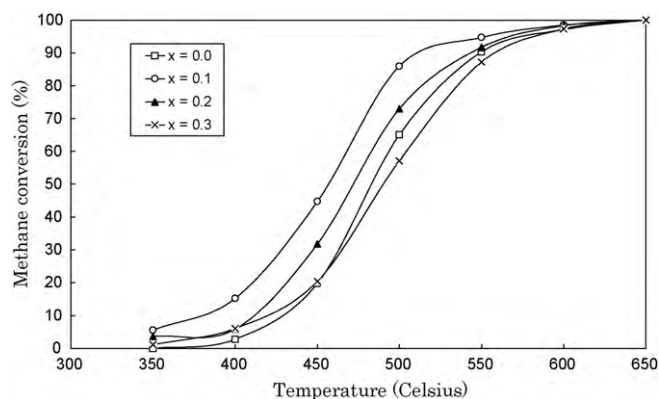
### 3.2. Effect of the degree of substitution

As described above, the oxide  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_{3-\delta}$  prepared by the urea decomposition method had the best catalytic activity for methane combustion, thus this method was further applied to prepare other oxides  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  with nominal degree of substitution  $x = 0.0, 0.2$  and  $0.3$ . Calcination of the precursors was kept at the identical condition of 700 °C for 5 h. Catalytic activities of the oxides  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.0, 0.1, 0.2, 0.3$ ) for methane combustion are compared in Fig. 4. It is seen that the oxide with  $x = 0.1$  has the highest activity for methane combustion. Catalytic activity of the oxides is in order of  $x = 0.1 > x = 0.2 > x = 0.0$  and  $x = 0.3$  (when methane conversion was higher than 20%,  $x = 0.0 > x = 0.3$ ). Forni et al. prepared three samples of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.0, 0.2$  and  $0.4$ ) by a citrate method, and observed an activity order of  $x = 0.2 > x = 0.0 > x = 0.4$  [10]. It is similar to ours.

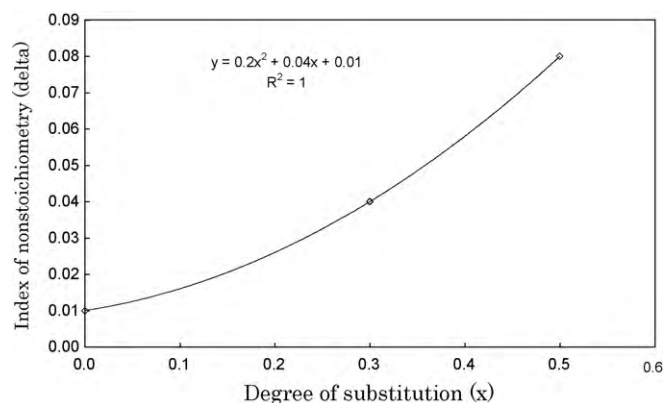
Fig. 5 shows XRD patterns of the oxides with nominal degree of substitution  $x = 0.0, 0.1, 0.2, 0.3$  and calcined at 700 °C for 5 h. It



**Fig. 3.** X-ray photoelectron spectra of La 3d<sub>5/2</sub> of the oxides (with molar ratio of La/Sr/Co = 0.9/0.1/1.0) prepared by the four methods and calcined at 700 °C for 5 h (a) urea decomposition method, (b) citrate method, (c) precipitation method using ammonia as precipitant, (d) precipitation method using carbonate as precipitant.



**Fig. 4.** Effect of nominal degree of substitution ( $x$ ) on methane conversion observed over the oxides (with molar ratio of La/Sr/Co =  $(1-x)/x/1.0$ ) prepared by the urea decomposition method and calcined at the identical condition of 700 °C for 5 h.



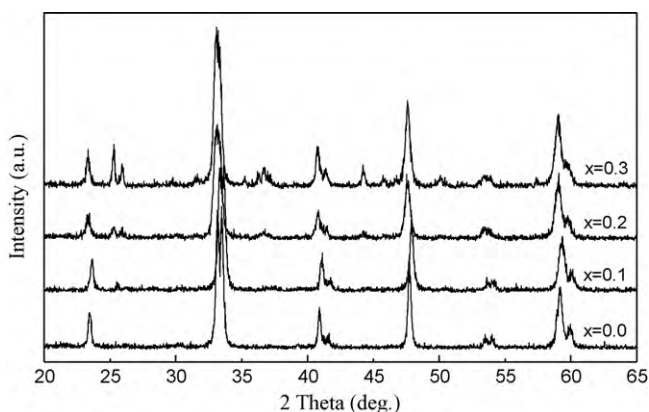
**Fig. 7.** Index of non-stoichiometry of lattice oxygen versus degree of substitution in the perovskite-type  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  oxides reported in Ref. [23].

**Table 4**

Index of non-stoichiometry of lattice oxygen ( $\delta$ ) and distribution of cobalt ions in the perovskite-type  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  oxides estimated from the simulation curve ( $\delta = 0.2x^2 + 0.04x + 0.01$ ) shown in Fig. 7.

$x$	$\delta$	Average $n$ of $\text{Co}^{n+}$	Distribution in percentage			SSA <sup>a</sup> ( $\text{m}^2/\text{g}$ )
			$\text{Co}^{2+}$	$\text{Co}^{3+}$	$\text{Co}^{4+}$	
0.0	0.010	2.980	2.0	98.0	0.0	5.9
0.1	0.016	3.068	0.0	93.2	6.8	10.0
0.2	0.026	3.148	0.0	85.2	14.8	–
0.3	0.040	3.220	0.0	78.0	22.0	7.4

<sup>a</sup> SSA is specific surface area of the oxides (with molar ratio of La/Sr/Co =  $(1-x)/x/1.0$ ) prepared by the urea decomposition method and calcined at 700 °C for 5 h.

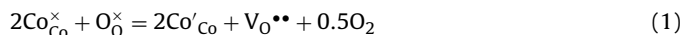


**Fig. 5.** XRD patterns of the oxides (with molar ratio of La/Sr/Co =  $(1-x)/x/1.0$ ,  $x = 0.0, 0.1, 0.2, 0.3$ ) prepared by the urea decomposition method and calcined at the identical condition of 700 °C for 5 h.

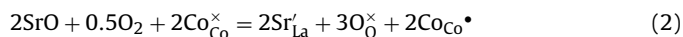
is seen that as degree of substitution ( $x$ ) increases,  $\text{SrCo}_3$  phase ( $2\theta = 25\text{--}26^\circ$ ) appeared more evident. And also when  $x = 0.3$  the phase of  $\text{Co}_3\text{O}_4$  oxide was visible ( $2\theta = 36.9, 44.8^\circ$ ). As shown in Fig. 6, simple oxide  $\text{Co}_3\text{O}_4$  had a higher catalytic activity at lower temperatures, which would be a reason for the activity order of  $x = 0.3 > x = 0.0$  in the range of  $\text{CH}_4$  conversion less than 20% for the oxide catalysts (see Fig. 4).

Borovskikh et al. prepared perovskite La–Co samples by using a freeze-drying method [23]. They reported the index of non-

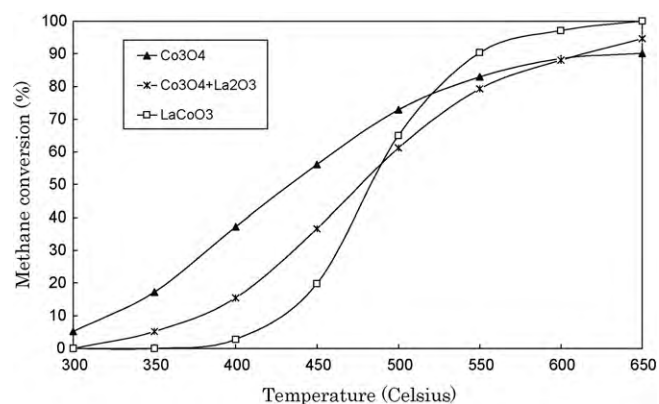
stoichiometry of lattice oxygen ( $\delta$ ) being 0.01 for the  $\text{LaCoO}_{3-\delta}$  sample. The  $\delta$  value reflects extent of vacancy of lattice oxygen in the whole solid. Formation of the lattice oxygen vacancy can be expressed in reaction (1) according to Kroger–Vink notation.



For the partially substituted perovskite  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  oxide they found that the index of non-stoichiometry of lattice oxygen ( $\delta$ ) increased with degree of substitution ( $x$ ) increasing, which is shown in Fig. 7. Owing to substitution of strontium ion for lanthanum ion, reactions (2) and (3) took place to preserve electrical neutrality of the crystal structure.

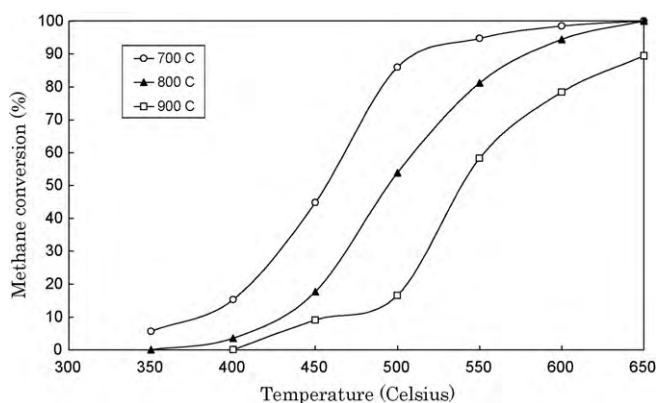


These two processes would occur at certain probabilities. Table 4 gives the estimated values of the index of non-stoichiometry of lattice oxygen ( $\delta$ ) and distribution of cobalt ions in the  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  oxides from the simulation curve shown in Fig. 7. The oxides prepared in the present work may differ from those of Borovskikh et al. But, the oxides  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.0, 0.1, 0.2, 0.3$ ) prepared by the urea decomposition method and calcined at 700 °C for 5 h all had main phase of perovskite (see Fig. 5). It is thus inferred that as  $x$  value increased, more  $\text{Sr}^{2+}$  ions had inserted into the A site of the perovskite structure. In Table 4 it is seen that as more  $\text{Sr}^{2+}$  inserted into the A site, both index of non-stoichiometry of lattice oxygen ( $\delta$ ) and percentage of  $\text{Co}^{4+}$  ion in oxide bulk increased. Since a larger  $\delta$  value means more sites of vacancy of lattice oxygen present in oxide bulk, it can be considered that an oxide with a larger  $\delta$  value would have more surface lattice oxygen vacancy. Lattice oxygen vacancy on surface of oxide is available to activate gaseous oxygen molecules into surface active oxygen species, and the surface active



**Fig. 6.** Comparison in the catalytic activity of the oxides prepared by the urea decomposition method and calcined at the identical condition of 700 °C for 5 h (the  $\text{Co}_3\text{O}_4 + \text{La}_2\text{O}_3$  catalyst is a physical mixture of  $\text{Co}_3\text{O}_4$  (180 mg) with  $\text{La}_2\text{O}_3$  (420 mg)).

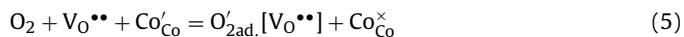
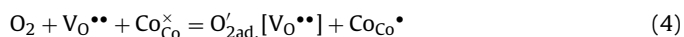




**Fig. 8.** Effect of calcination temperature (700, 800, 900 °C) on catalytic activity of the oxide (with molar ratio of La/Sr/Co = 0.9/0.1/1.0) prepared by the urea decomposition method (calcined for 5 h at each temperature).

oxygen species is able to oxidize methane molecules into CO<sub>2</sub> and H<sub>2</sub>O molecules.

Activation process of gaseous oxygen on surface lattice oxygen vacancy would need an extent of electron transfer, i.e., require cooperation with neighboring cobalt ions at a lower oxidation state, such as those depicted in reactions (4) and (5).



The  $\text{O}_{2\text{ad}}^{\times}$  species adsorbed at the site of surface lattice oxygen vacancy might in similar way get more electrons further from the surrounding cobalt ions at lower oxidation states. But, if there are excessive number of Co<sup>4+</sup> ions surrounding a site of surface lattice oxygen vacancy, gaseous oxygen adsorbed at the site of vacancy is not feasible to get electrons from the surrounding cobalt ions. For this reason, appropriate concentrations of surface lattice oxygen vacancy and cobalt ions at lower oxidation states are both necessary to activate gaseous oxygen into negatively charged surface active oxygen species.

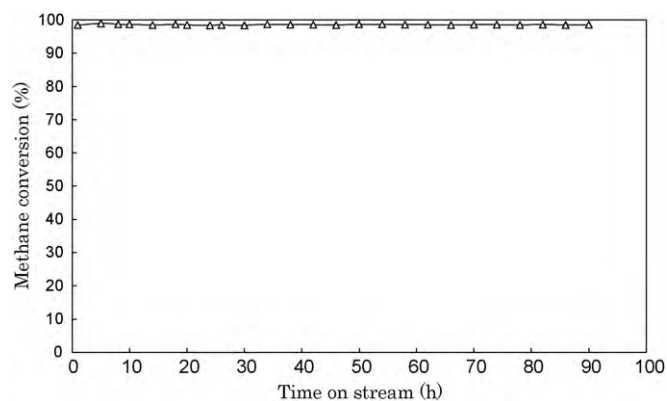
Our experimental results indicate that the surface structure of the oxide with nominal degree of substitution  $x = 0.1$  are optimal for methane oxidation. Deviating from  $x = 0.1$  led to a reduced catalytic activity as shown in Fig. 4. The fact may imply that the oxide with  $x = 0.0$  was insufficient in oxygen vacancy, and the oxide with  $x = 0.3$  was excessive in number of Co<sup>4+</sup> ions which was disadvantageous to activation of gaseous oxygen.

### 3.3. Effect of calcination temperature

To investigate effect of calcination temperature, the precursor with molar ratio of La/Sr/Co = 0.9/0.1/1.0 prepared by the urea decomposition method was also calcined at 800 °C or 900 °C for 5 h. Based on XRD patterns, a completely single phase of perovskite structure was formed after the calcination at 900 °C for 5 h. Specific surface areas of the oxides La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3-δ</sub> are 10.0, 4.7 and 2.2 m<sup>2</sup>/g, corresponding to the calcination temperature 700, 800 and 900 °C, respectively. Catalytic activities for methane combustion of the oxides calcined at the three temperatures are compared in Fig. 8. It is obvious that higher temperature calcination led to a reduced methane conversion.

### 3.4. Thermal durability of the oxide La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3-δ</sub> catalyst

Thermal durability of the oxide La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3-δ</sub> catalyst prepared by the urea decomposition method and calcined at 700 °C for 5 h was investigated. Result is shown in Fig. 9. It is seen that



**Fig. 9.** Methane conversion versus time on stream at reaction temperature 600 °C over the oxide catalyst (with molar ratio of La/Sr/Co = 0.9/0.1/1.0) prepared by the urea decomposition method and calcined at 700 °C for 5 h.

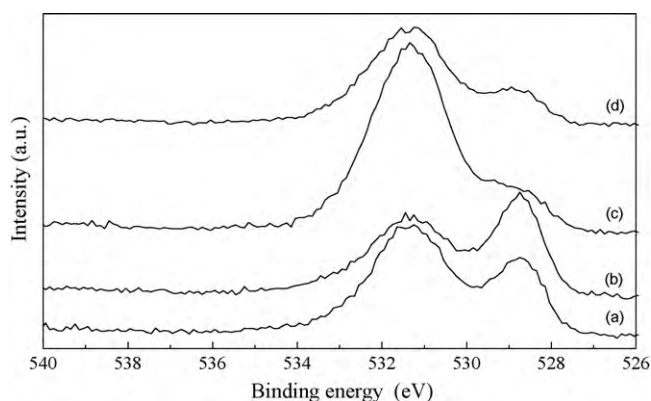
at reaction temperature 600 °C catalytic activity of the oxide was stable during the 90 h test, with methane conversion keeping at around 98.6%. This indicates that the urea decomposition method is good for preparation of the perovskite-type oxide catalyst for methane combustion.

### 3.5. Reconsideration for catalytic activity of the oxides prepared by the four methods

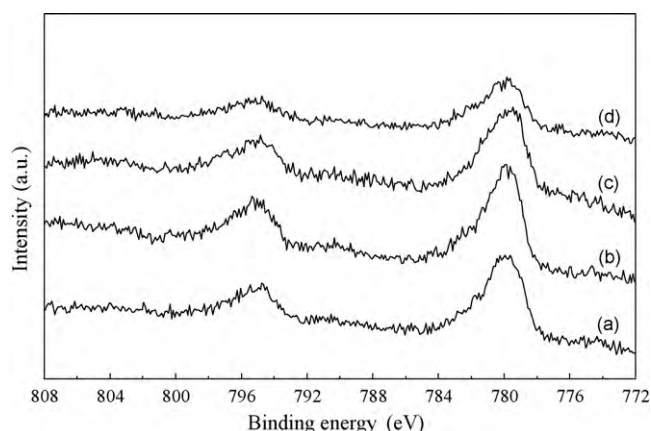
As stated above four methods were adopted to prepare the oxides with molar ratio of La/Sr/Co = 0.9/0.1/1.0, and all the precursors were calcined at the identical condition of 700 °C for 5 h. Catalytic activities for methane combustion of the four oxides thus obtained are shown in Fig. 1. It is obvious that preparation method had a great influence on the catalytic activity.

Based on Tables 2 and 3, surface layer composition of the (a) sample (with molar ratio of La/Sr/Co = 0.9/0.1/1.0 and calcined at 700 °C for 5 h) can be expressed as  $\{[\text{La}_{11.4}\text{Sr}_{3.0}\text{Co}_{6.3}\text{O}_{79.3} \times 0.267](\text{O}^*_{79.3} \times 0.733)\}$ . The part in square bracket belongs to surface layer crystalline structure, and the part in round bracket is surface non-lattice oxygen species. If one makes a first approximation to regard cobalt ion as constant +3, the surface non-lattice oxygen species has an average negative charge of 0.288 electrons per O<sup>\*</sup> species. Furthermore, if one prefers to regard the surface non-lattice oxygen species in dioxygen form, the surface non-lattice oxygen species will be a mixture of  $\text{O}_{2\text{ad}}^{\times}$  and  $\text{O}_{2\text{ad}}$  species, in which 28.8% in  $\text{O}_{2\text{ad}}^{\times}$  form and 71.2% in  $\text{O}_{2\text{ad}}$  form. Similar estimation can be applied to other samples.

In fact, the surface non-lattice oxygen species may not necessarily be all in dioxygen form. Fig. 10 is O 1s X-ray photoelectron spectra of the oxides (with molar ratio of La/Sr/Co = 0.9/0.1/1.0) prepared by the four methods and calcined at 700 °C for 5 h. The oxygen species with O 1s binding energy at 531.3 eV can be assigned to  $\text{O}_2^-$  or  $\text{O}^-$  species, and also to hydroxyl groups and carbonate groups [24,25]. It is a fact that all the oxides had surface carbonate groups, which had been proved by C 1s X-ray photoelectron spectra. Moreover, the (c) and (d) samples were prepared by precipitation method using alkaline solutions as precipitants, and presence of La<sub>2</sub>O<sub>3</sub> phase was recognized in XRD patterns as shown in Fig. 2. Fig. 3 would be a proof for presence of surface hydroxyls on the (c) and (d) samples. It is reported that lanthanum hydroxide and lanthanum oxide have a shifted peak position of La 3d<sub>5/2</sub> binding energy in X-ray photoelectron spectra to the perovskite oxides [22]. On the other hand, number of surface oxygen species is changed with temperature [26], so catalytic cycle of surface oxygen species in methane oxidation is certainly related to reaction temperature. At a higher temperature, only a reduced number of sites of sur-



**Fig. 10.** X-ray photoelectron spectra of O 1s of the oxides (with molar ratio of La/Sr/Co = 0.9/0.1/1.0) prepared by the four methods and calcined at 700 °C for 5 h (a) urea decomposition method, (b) citrate method, (c) precipitation method using ammonia as precipitant, (d) precipitation method using carbonate as precipitant.



**Fig. 11.** X-ray photoelectron spectra of Co 2p of the oxides (with molar ratio of La/Sr/Co = 0.9/0.1/1.0) prepared by the four methods and calcined at 700 °C for 5 h (a) urea decomposition method, (b) citrate method, (c) precipitation method using ammonia as precipitant, (d) precipitation method using carbonate as precipitant.

face lattice oxygen vacancy can effectively activate gaseous oxygen. This is because only stronger adsorption binding is able to compensate for desorption activity of oxygen species on surface at high temperatures.

Thus, it is certain that an appropriate surface structure and composition of oxide catalyst is important to achieve a high catalytic activity. In the case that surface active oxygen species for methane oxidation is negatively charged oxygen species, redox mechanism containing transformation of  $\text{Co}^{3+}$  with  $\text{Co}^{4+}$  on the oxide is present. Presence of  $\text{Co}^{4+}$  ions in perovskite  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  oxides had been confirmed with chemical analyses by many authors [23,27,28], and the percentage of  $\text{Co}^{4+}$  ions was found to be increasing with the degree of substitution ( $x$ ). In the present work, X-ray photoelectron spectra of Co 2p of the oxides (with molar ratio of La/Sr/Co = 0.9/0.1/1.0) prepared by the four methods and calcined at 700 °C for 5 h were collected and shown in Fig. 11. The main peaks at 780.0 eV (Co 2p<sub>3/2</sub>) and 794.8 eV (Co 2p<sub>1/2</sub>) are indicative of prevailing presence of  $\text{Co}^{3+}$  ions. But, an amount of  $\text{Co}^{4+}$  ions should also be present in the surface layers of the perovskites in the light of the results of chemical analyses [23,27,28]. Since the main phase of the oxides was perovskite phase,  $\text{Co}^{2+}$  ion was only possible to be present in the minor phase of  $\text{Co}_3\text{O}_4$ , which was hardly observed in the (a) sample (see Fig. 2). Dupin et al. studied the positive electrode material  $\text{Li}_{0.66}\text{CoO}_2$  by XPS and assigned the binding energies of 781.5 eV (Co 2p<sub>3/2</sub>) and 796.8 eV (Co 2p<sub>1/2</sub>) to  $\text{Co}^{4+}$  ion [29]. Simi-

lar to Ref. [29], curve fitting of the Co 2p<sub>3/2</sub> peaks in Fig. 11 by use of the XPS data of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions was tried. Unfortunately, due to the small difference (ca. 1.5 eV) in binding energy of the two types of cobalt ion, estimation of cobalt ion distribution had a large uncertainty. More detailed study of  $\text{Co}^{4+}$  distribution in oxide bulk and surface layer will be carried out on pure phase perovskite oxides obtained at high calcination temperatures such as 900 °C in future.

#### 4. Conclusions

Four methods were adopted to prepare perovskite-type oxides with molar ratio of La/Sr/Co = 0.9/0.1/1.0. At the same calcination condition of 700 °C and 5 h, the urea decomposition method produced predominantly perovskite phase oxide, with a minor of  $\text{SrCO}_3$  phase formed. Whereas the two precipitation methods produced samples containing  $\text{La}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  phases evidently. The citrate method could also produce predominantly perovskite oxide, but the oxide prepared by the citrate method was inferior to the oxide prepared by the urea decomposition method in activity of catalytic combustion of methane.

The oxide prepared by the urea decomposition method and calcined at 700 °C for 5 h had the highest catalytic activity for methane combustion, which was ascribed to its unique surface features, including surface layer composition, concentration of surface lattice oxygen vacancy, molar ratio of surface lattice oxygen/cobalt ion. Moreover, the oxide also exhibited a good thermal stability as catalyst for methane combustion. During the 90 h test at reaction temperature 600 °C, methane conversion was kept at around 98.6% without any decline.

Due to the highest activity of the oxide  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_{3-\delta}$  prepared by the urea decomposition method, other oxides  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  with nominal degree of substitution  $x = 0.0, 0.2, 0.3$  were also prepared under the identical calcination condition of 700 °C and 5 h. It is found that catalytic activity for methane combustion of the oxides is in order of  $x = 0.1 > x = 0.2 > x = 0.0$  and  $x = 0.3$ . This indicates that activation of gaseous oxygen is dependent on proper concentrations of lattice oxygen vacancy and cobalt ion at lower oxidation states on the surface of the oxide catalysts.

When the precursor with molar ratio of La/Sr/Co = 0.9/0.1/1.0 prepared by the urea decomposition method was calcined at 900 °C for 5 h, a completely single phase of perovskite oxide  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_{3-\delta}$  (as verified by XRD) was obtained. This indicates that the urea decomposition method is a proper method to prepare pure phase perovskite oxide under a relatively mild calcination condition.

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